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Progress towards highly stable and lead-free perovskite solar cells

Muhazri Abd Mutalib¹ · Norasikin Ahmad Ludin¹ · Nik Ahmad Aizudden Nik Ruzalman² · Vincent Barrioz² · Suhaila Sepeai¹ · Mohd Asri Mat Teridi¹ · Mohd Sukor Su'ait¹ · Mohd Adib Ibrahim¹ · Kamaruzzaman Sopian¹

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Abstract

High-performance perovskite solar cells have attracted increased attention for photovoltaic applications and potentially replacing the predecessor generations. Nevertheless, the stability issues and the lead content has always been among the major concerns that barriers perovskite solar cells from commercialization. This review presents the discussion towards the inherent instability of perovskite solar cells and the development towards replacing lead with discussion towards their performance and challenges. The degradation of perovskite active layer would release toxic substance into the environment. The development towards low-toxic, lead-free and efficient perovskite solar cells is the key for a sustainable solar energy generation with the application of perovskite solar cells.

Keywords Perovskite solar cells · Lead-free perovskite · Moisture-stability · Sn perovskite · Power conversion efficiency

Introduction

The interest of power conversion from light source has been on the rise over the years as an alternative energy generation technology since it is considered as natural, renewable, clean, safe as well as free from negative side impacts to human and nature. Even though current photovoltaic market is dominated by first generation silicon solar cell by 80–90% with highest recorded efficiency at Standard Test Condition (STC) above 25% [1, 2], second generation Thin Film solar cell is rapidly approaching behind at current highest efficiency based on STC positioning CIGS and CdTe based thin film at 22.6 and 22.1%, respectively [3].

Even with the advantages of first generation solar cell, the production cost is still higher than the other generations and 50% of the cost is originated from the price of the silicon wafer itself [4]. In contrast to silicon solar cell, lesser material is needed to produce thin film solar cell and the

production of thin films does not require complicated processing steps as compared to silicon solar cell. The production cost is much lower and this is one of the main advantages for this technology to outrun the existing solar cell technology [5]. Currently, ongoing research for thin film absorber material is much focusing on CdTe solar cells considering these materials permits high-efficiency and stability [6]; however, due to the fact that limited availability and rising cost of Te with projected demand for PV module is high [7], a new material as an absorber layer is needed to replace these material.

From the concept of thin film, in 1991, Michael Graetzel introduced the architecture of Dye Sensitized Solar Cell (DSSC) and it is categorized into third generation solar cell. Similar to the thin film solar cell, DSSC also possess several advantages that is closing the gaps between existing silicon solar cell technology such as low-manufacturing cost, eco-friendliness, availability, and simple manufacturing requirements. Other than the architecture of 'Dye' and 'Sensitizer' in DSSC, the difference between DSSC and thin film solar cell is the involvement of redox couple to assist the light-power conversion. While there are researches focusing on the stability of DSSC [8], other research groups are also focusing on the fabrication technique [9, 10], material for counter electrode [11, 12] and alternative material for the sensitizer to improve its

✉ Norasikin Ahmad Ludin
sheekeen@ukm.edu.my

¹ Solar Energy Research Institute (SERI), Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

² Department of Physics and Electrical Engineering, Northumbria University, Ellison Building, Newcastle upon Tyne NE1 8ST, UK

explicitly, such as CdS, Ag₂S, CdTe, CdHgTe, InAs, PbS, TiO₂, ZnO and carbon-based species [13].

The incorporation of perovskite material into DSSC as the sensitizer layer marks the beginning of Perovskite Solar Cell (PSC) advancement and it is a promising technology for future power generation from solar irradiation. PSC has attracted interest from many researchers due to its ease of fabrication steps, low-cost starting material, high-efficiency and able to outperform DSSC as well as conventional solar cells. Figure 1a shows the introduction of perovskite material in DSSC where it functions as a replacement for the dye sensitizer for the mesoporous TiO₂ layer. In this type of architecture, the working concept is the same with normal DSSC where it is by redox couple and recorded efficiency is 9.7% [14]. The incorporation of perovskite material in DSSC is almost similar to the concept of quantum dot (QD) solar cell [15].

Previous study had fabricated a non-sensitized PSC using mesoporous Al₂O₃ to support the perovskite layer [16]. The unique criteria of perovskite material can be observed in this study with the solar cell structure as in Fig. 1b, where it was proven that the electron was not injected into the Al₂O₃ layer, instead it is transported through the perovskite layer to the electrode layer. This is due to the higher electron mobility in perovskite compared to Al₂O₃ layer, at 25 and 7.5 cm²V⁻¹S⁻¹, respectively [16]. Based on this observation, two preliminary conclusions were outlined; electron transportation is possible in the perovskite material and it is not necessary to include electron transport material (ETM) in PSC [14]. This is where the cell structure of PSC leads to planar perovskite solar cells as in Fig. 1d. The planar design allowed the PSC to be fabricated without the TiO₂ layers which requires annealing at high temperature. Nevertheless, some research group still employs the mesoscopic perovskite solar cells (Fig. 1c) due to the reported disadvantages of planar architecture which includes high-density of trap states and more severe hysteresis phenomenon compared to the mesoscopic perovskite solar cells [17].

Planar architecture PSC was then further developed into inverted structure. In inverted structure, we would observe the order of electrodes is flipped into *p-i-n* junction and hole transport layer (HTM) is deposited before the perovskite material [18]. It was reported that the inverted design had allowed facile and cost-effective of fabrication [18]. This review, however, will be focusing towards the mesoporous PSC and planar PSC. Planar PSC can be processed at low temperature, due to the absence of high temperature processed TiO₂, has been able to achieve high power conversion efficiency close to mesoporous PSC [19, 20]. Nevertheless, previous study had overcome the high temperature processed TiO₂ by employing atomic layer deposition of TiO₂ layers with low temperature plasma [21]. This development had enable the fabrication of PSC devices on a flexible plastic substrate and showed that mesoporous PSC can possibly be produced without the high temperature annealing process.

Despite the advantages of PSC, there are several drawbacks of this architecture. One of the most concerning is the cell's efficiency and stability. Since solar cell is considered as a waste of electrical and electronic equipment [22], it is important to consider stability issues to commercialize this technology. Very few stability studies have been conducted to date [23]. It can be shown directly from the graph obtained from NREL where researchers worldwide are trying to increase the efficiency of PSC from 3.8% (2009—Toin University) to 21.1% [3, 24]. More and more researches is ongoing as this paper was completed. However, this yearly highest recorded efficiency for PSC that is recognized by NREL is so far involves lead-based material. The first recorded PSC with power conversion efficiency (PCE) at 3.8% is lead-based material [24]. As for KRICT in their 2013, 2014, and 2015 record, they are using lead-based Perovskite material [3], the only difference between these record-breaking PSC is the fabrication process. Details about this fabrication process are yet to be published by them. Research by Oxford University in 2013 is also lead-based material. Research that incorporates lead-based PSC have been shown by many as shown in Table 1, this table

Fig. 1 Incorporation of perovskite material from the earliest cell design (a DSSC) to existing design (d Perovskite solar cell) [14]

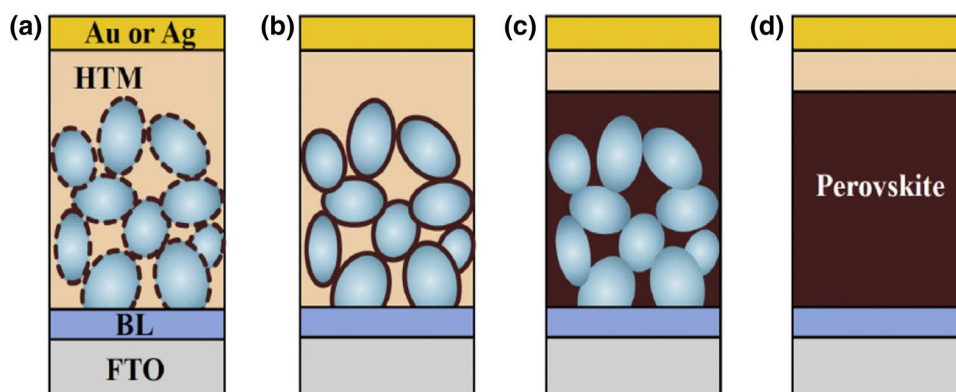


Table 1 Some of the recent research activities on PSC that involve lead-based material

References	Year	Objectives	Absorber material	ETM/HTM material	Fabrication technique	Result
[25]	2016	Incorporation of quadruple cation perovskite absorber layer	RbCsMAFAPbI ₃	Spiro-OMeTAD with poly(triarylamine)	Spin coating	Stabilized efficiency of 21.6%
[26]		Studying the absorber layer formation during the annealing of perovskite precursor film	CH ₃ NH ₃ PbI _{3-x} Cl _x	Spiro-OMeTAD	Spin coating	Two types of grain formation were identified and PCE is at 15.7%
[27]		Amine free PSC with additional hole extraction layer insertion	CsPbI ₃	Spiro-OMeTAD	Spin coating	Efficiency enhancement from 0.09 to 4.68%
[28]	2015	Preparation of formamidinium lead iodide perovskites solar cells	FAPbI ₃	Poly(triarylamine)	Spin coating	Power conversion efficiency of 20.1% was recorded
[29]		Study the effect of thermal annealing onto absorber material	CH ₃ NH ₃ PbI ₃	Spiro-OMeTAD	Spin coating	Annealing temperature will effect device lifetime and yield difference electrical parameters
[30]		To produce PSC in ambient air without high vacuum assisted processing	CH ₃ NH ₃ PbI ₃	Spiro-OMeTAD	Double-step vapour assisted spin coating	PCE is at 12.7% with the advantages of storing at 50% humidity at temperature 20oC for 14 days
[31]		Study the atmospheric effect on PSC (Vacuum, dry nitrogen and dry air) for storage and fabrication purposes.	CH ₃ NH ₃ PbI _{3-x} Cl _x	Spiro-OMeTAD	Spin coating	Dry air was found to be the most favourable atmosphere for PSC with PCE at 11.2%
[32]		To test PSC with different HTM by simulation	CH ₃ NH ₃ PbI ₃	Spiro-OMeTAD, Cu ₂ O, NiO, CuI, CuSCN	N/A	Cell with Cu ₂ O as HTM outperform every other HTM material
[33]		To fabricate PSC using one-step CVD method	CH ₃ NH ₃ PbI ₃ and CH ₃ NH ₃ PbI _{3-x} Cl _x	Spiro-OMeTAD	Gas assisted CVD	Large grain size at average 1 micrometre with PCE at 11.1%
[34]		To produce PSC via sequential deposition spin coating	CH ₃ NH ₃ PbI ₃	Spiro-OMeTAD	Sequential deposition spin coat	Mesostructured PSC with PCE at 11.3%
[35]	2015	Producing PSC with precursor dependent morphology	CH ₃ NH ₃ PbI ₃	Spiro-OMeTAD	Spin coating with excessive precursor	Excessive precursor positively affects absorber film formation. PCE at 16.1% were obtained
[36]		To investigate the effect of different photoanode thickness to HTM free PSC	CH ₃ NH ₃ PbI ₃	N/A	Magnetron sputtering	Discovered that thin photoanode (thickness of 0.8 µm) poses high electron lifetime thus reducing charge recombination, efficiency of 12.22% were obtained
[37]		To investigate charge carrier transport in HTM-free PSC	CH ₃ NH ₃ PbI ₃	N/A	Spin coating	Recombination in FTO based PSC is mainly due to the combined influence of TiO ₂ -Perovskite and perovskite-carbon interfaces
[38]		To produce and study PSC that were produced under ambient air conditions	CH ₃ NH ₃ PbI ₃	Spiro-OMeTAD	Spin coating	Obtained efficiency at 7%. Overall results is at satisfactory level

Table 1 (continued)

References	Year	Objectives	Absorber material	ETM/HTM material	Fabrication technique	Result
[39]	2014	Developed anti-solvent method for spin coating of perovskite layer	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Poly(triarylamine)	Spin coating with toluene quenching	Certified efficiency of 16.2% was recorded
[40]		Compared one-step and two step method for perovskite absorber layer	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Spiro-OMeTAD	Spin coating	Two step method produced layer with better fill factor and higher voltage
[41]		Controlling the absorber morphology by applying surfactant	$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$	Spiro-OMeTAD	Spin coating	Efficiency enhancement from 4.51 to 8.74%
[42]		Comparing spiro-OMeTAD with P3HT as HTM	$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$	Spiro-OMeTAD and P3HT	Spin coating	Highest recorded PCE with P3HT as HTM —9.3%
[43]		Studying HTM free PSC using simulation by looking onto band offset in PSC (conduction band offset and valence band offsets)—planar type cell	$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$	Spiro-OMeTAD and HTM free	N/A	Conduction band offset lower than absorber— V_{oc} decreased due to interface recombination become prominent

eventually shows the current prospects of PSC research and it focus on the absorber material and some other parts in PSC were also considered. Their efficiency was at very satisfying level, but seldom address the issue of environmental impact that can be caused by the device.

The toxicity issues due to lead had also been a major obstacle to commercial application of perovskite solar cells. There are complications associated with the environment and human health when lead-based materials are used in perovskite solar cells. Human exposure to lead can cause brain malfunction, premature infants and low birth rate, circulatory system damage and kidneys malfunctioning. Not only to humans, lead can also cause negative impacts to the environment as well as aquatic life. Current situations have urged researchers to focus on obtaining record-breaking efficiency of PSC, but without seriously addressing the environmental impact that lead can cause. Lead-free PSC will be undeniably crucial if this technology is to be commercialized and to compete with existing PV technologies.

As current publications have address the toxicity issue of lead [23, 44–47], increasing number of researchers have attempt to find suitable replacement of lead in PSC [48–50]. Most notably, Sn-based perovskite had been viewed as the most suitable replacement due to its similar chemical nature to Pb as group 14 metal. Nevertheless, the stability issues of Sn with self-doping had limits the development of Sn-based perovskite [51]. This issue can potentially be managed by adding SnF_2 as inhibitor towards the formation of Sn^{4+} [51]. Additionally, encapsulation also improves the overall device stability which had been proven to be able to maintain 98% of its power conversion efficiency over 100 days. Thus, there are huge potential for the development of other materials as replacement for the highly toxic lead to produce lead-free perovskite solar cells with high-efficiency.

Cell structure and working mechanism of PSC

The common working principle of any existing solar cell is energy absorption from light source, electron–hole separation, charge collection and electron–hole recombination. Although the exact working principle of PSC is not very well understood at the time being [46, 50], the most simple and reliable explanation is as described by Park et al. in Fig. 2 [44]. Photon with enough energy is emitted onto the PSC surface and its energy is absorbed by the absorber. Electron–hole pair will be produced due to the difference in electric field applied by the electrodes, the electron and hole will be attracted, thus movement of the electron will produce electricity.

Due to the unique advantages of perovskite material which possess the ability to transport electron and hole, as

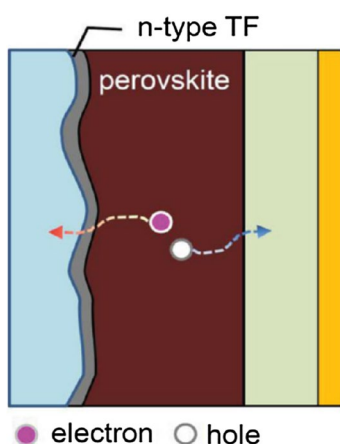


Fig. 2 Schematic diagram of working principle for PSC [42]

showed by previous study which simulated the possibility of forming a PSC without HTM [43]. This cell pattern, however, depends on the work function of the back contact with energy of the valence band ($E_{v_absorber}$). This simulation is further supported experimentally by another literature [37]. Although HTM-free PSC is possible, several other researchers proved the importance of having a HTM in PSC is rather important and could affect to a positive increment of several outcomes namely PCE, FF, V_{oc} , decreases the internal resistance of the cell as well as increases the electron lifetime thus promoting electron collection and indirectly preventing electron–hole recombination.

Material and stability of PSC

Initially, perovskite material is used as sensitizer in dye sensitized solar cell (DSSC) and it is generally in the form of Organolead Halide. The general formula for perovskite is AMX_3 , where A is Akyl Ammonia cation (ex: $CH_3NH_3^+$), M is metal cation (ex: Pb^{2+}) and X is Halide Anion (ex: Br^- , I^- or Cl^-). According to previous research, formability of perovskite material is based on distance ratio between Akylammonia cation–Halide Anion and metal cation–halide anion (A:X and M:X) [13]. This ratio is known as tolerance factor (TF) [52] and the formula is as below:

$$TF = (R_A + R_B) / [\sqrt{2(R_B + R_X)}]$$

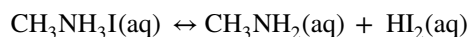
An ideal perovskite material possess $TF=1$, where the molecular structure is perfect cubical. Distorted octahedral is to be expected when $TF < 1$ and this might affect the electronic properties of the material. Thus, the best material to form PSC is small cation ‘A’ that retain ionic radius within the range of 1.60 Å–2.50 Å will form Perovskite material, thus, Methylammonia, $CH_3NH_3^+$ (1.80 Å), Ethylammonia,

$CH_3CH_2NH_3^+$ (2.30 Å) and Formamidinia, $NH_2CH=NH_2^+$ (1.90–2.20 Å) is found to be the most suitable material [15, 53].

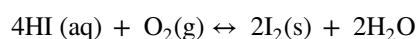
The most common perovskite material currently used is methylammonium lead halide ($CH_3NH_3PbX_3$, X=F, Cl, Br or I), which have suitable optical and electronic properties [23]. The basic steps to produce this solar active layer are to react PbI_2 with CH_3NH_3I . Keeping in mind that this reaction is reversible, in one direction is the formation of perovskite film itself and if reversed, is the decomposition to PbI_2 . The formation of water soluble PbI_2 during the decomposition of perovskite material is the main obstacle that prevents commercialization of perovskite solar cells. Other than humidity, UV-light, solution (perovskite compositions), oxygen and temperature are among the factors that can cause PSC degradation [47, 54–58]. Degradation of PSC due to humidity is described in the following chemical reaction [45]:



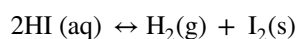
Upon contact with humidity, the hygroscopic methylammonium iodide (MAI) is separated from Perovskite crystal and combines with iodine forming aqueous MAI and solid PbI_2 . In further reaction with humidity, MAI will subsequently decompose to aqueous methylamine, $CH_3NH_3(aq)$ and hydriodic acid, $HI(aq)$:



In contact with oxygen, HI will degrade and produce H_2O and I_2 as below equation:



Should the photochemical reaction with UV took place; the reaction will proceed as below:



In addition of humidity, UV-light, solution (perovskite compositions), oxygen and temperature, other related factors were also discovered to affects the solar cells stability. Previous research has found that storage conditions also have an influence over perovskite solar cells stability [59]. Dry air was found to be the most suitable storage atmosphere (during the drying process of HTM) if Spiro-OMeTAD act as the HTM in the cell. Solar device architecture also eventually affects the cells stability. Jose and co-workers found that scaffold structured electron transport layer (ETL) produces better stability than planar structured layer [60]. These two devices, Planar and Scaffold (Fig. 3), were compared in the same controlled atmosphere.

In another study, different ETMs; Spiro-OMeTAD, NiO, CuI, CuSCN and Cu_2O , were compared for the most outstanding result with different thickness setting for ETM, absorber layer as well as HTM [32]. It was understood that humidity can cause degradation of PSC. However, using Cu_2O as the ETM, it was observed that cell degradation

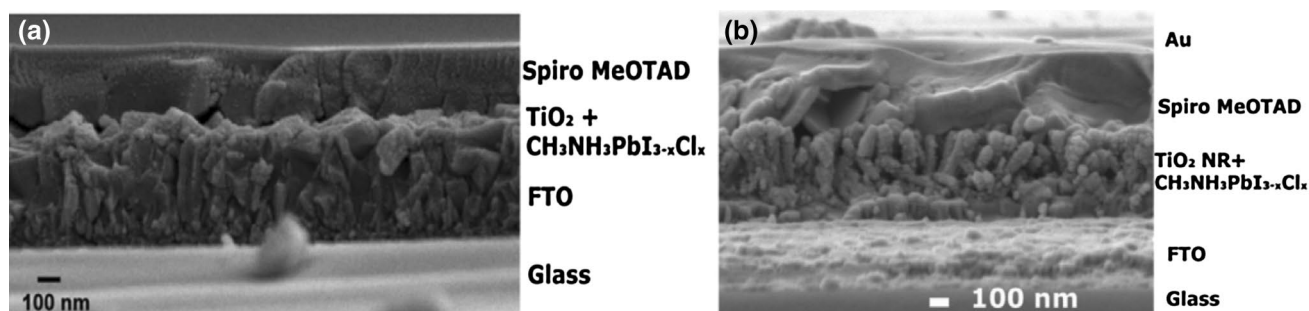


Fig. 3 Planar type cell (a) and Scaffold type cell (b) [40]

caused by moisture can be avoided while maintaining high electron mobility. Cells with Cu_2O outperform every other ETM. Recent study has also added reduced graphene oxide (rGO)/mesoporous (mp)- TiO_2 nanocomposite based meso-structured perovskite solar cells [61]. The study had demonstrated the improvement in electron transport property and photon conversion efficiency which is contributed by the reduction in resistance at interface.

Recent study has improved the performance and stability issue of PSC by crystal crosslinking with alkylphosphonic (butylphosphonic) acid ω -ammonium chlorides (4-ABPACI) [62]. Through one-step solution processing, spin-coating (which in authors opinion, this is the easiest and most favourable way to fabricate PSC in which, if this method is proved success in producing high-efficiency and high stability PSC would take this technology a wide step forward in commercializing PSC), this team modified the surface of Methylammonium Lead Triiodide in the presence of alkylphosphonic acid ω -ammonium chlorides as the crosslink between neighbouring grains in the perovskite structure. 4-ABPACI act not only to increase the cells efficiency from 8.8 to 16.7%, but also enhancing its stability against moisture. Using XRD spectra before and after moisture test (comparing Pristine and 4-ABPACI deposited on mp- TiO_2/FTO), Pristine cells suffer from severe corrosion compared to 4-ABPACI cells. Other moisture barrier such as carbon cathode or Al_2O_3 is also quite suitable; however, it might be not suitable enough for widespread and long term stability, more extensive stabilizer is required.

Encapsulation method has also been proven to be able to influence the stability of PSC. When two encapsulation techniques were compared, it was demonstrated that stability of PSC fabricated with encapsulation adopted from organic light emitting diode (OLED) technology was able to yield improved stability under high humidity environments compared to typical UV curable epoxy resin method [63]. It was stated that the OLED method uses a desiccant material that absorbs water that may penetrate through the epoxy resin sealant.

Wang and co-workers said that in order for thin film solar cell to be fully commercialized, it is important that it complies with IEC 61646 testing standard which refers to environmental stability, which is at current research finding, this is the big thing to be solved [64]. In their paper, they address the stability issue based on the whole cell structure including the perovskite material itself, ETM and HTM layers, buffer layer as well as both of the electrodes. However, they stress more on the importance of the encapsulation layer while maintaining lead-based Perovskite material. Using lead-based perovskite is undeniably attractive due to high PCE as shown by many (as shown in Table 1). Nevertheless, controlling the stability only from the encapsulation will only reduce several percent of ecotoxicity from lead as the demand for lead is still available, which means the processing of lead is still exist. From authors' point of view, the best method to tackle this problem is to find a suitable replacement for lead to be used in PSC.

The above arguments can be supported by previous research [65]. For the first time, their team had reported the life cycle assessment (LCA) on ecotoxicity of PSC. Fabrication is based on two most successive reported articles on fabricating PSC that is Vapour Phase Deposition and Solution Processing. They concluded that the major contributor to negative environmental effect comes from the manufacturing process itself. The electricity required to fabricate the cell is the main arguments for this paper, and this by all means covers vapour and solution deposition. The only difference is the percentage of contribution between these two processing methods. Additionally, the life cycle impact analysis revealed that in both deposition processes, the impact was focused primarily on the human toxicity (cancer effect) and freshwater ecotoxicity, which is due to lead emission [65, 66]. However, the article suggested that PSC technology does not pose concern in its raw materials extraction, synthesis of the starting materials and manufacture of the PSC as compared to the other solar cell technologies. In another LCA, the research focuses on the difference of TiO_2 module and ZnO module for PSC [67]. The study found that both PSC modules have the shortest energy payback

time compared to the other solar cell technologies while emphasizing on reducing the high energy demand processes to lower the CO₂ emission factor.

Lead-free perovskite solar cell

Albeit the high-performance of PSCs with relatively high stability [68], the presence of lead has been taken into caution by the many researchers. The usage of such material has caused a relative concern due to obey strict requirement to be environmental friendly which hindered the large-scale implementation of perovskite solar cells. The main concern is circulated upon the possibility of solar modules would somehow crack under environmental hazards such as hail or earthquake, and thus releasing the degraded perovskite products into the environment [69]. Previous study had argued that the Pb content in PSC could deter market acceptance due to its risk towards human health and ecosystem [70]. To such extent, researchers are in the effort to replace Pb with other suitable materials to alleviate the toxicity issues in PSCs [71–75]. Suitable materials which have been proposed so far includes tin (Sn), bismuth (Bi), germanium (Ge) and copper (Cu) [76]. Table 2 summarizes the main research on lead-free perovskite and their performance.

Sn has been considered as a suitable substitution for Pb in perovskite solar cells due to their similarity in chemical properties [48, 49]. The use of Sn-based perovskite has been implemented in transistor with excellent charge motilities [88]. The application of Sn in perovskite solar cells usually involved the alloying of Sn/Pb with the recent study recording a 15% efficiency in oxygen deficient environment as well as in tandem applications [77, 89–91]. Ogomi et al. was one of the first to vary the composition of Pb:Sn ratio and tested the performance of perovskite solar cells [78]. They had proved the possibility of Sn could be a possible option as the

absorber material for solar cells, but also showed that pure Sn perovskite solar cells did not produce any photovoltaic performance. It was also demonstrated that Sn would able to intrinsically maintain its 2+ oxidation state with the presence of Pb in the absorber layer. Nevertheless, Snaith et al. has fabricated a totally Pb-free perovskite solar cells using MASnI₃ as the perovskite light absorber with encapsulation and in nitrogen environment glovebox to prevent the degradation of the Sn-based perovskite absorber [49]. The study also mentioned the stability issues of Sn-based perovskite where a discoloration was observed within seconds after the absorber layer was exposed to the ambient atmosphere due to the intrinsic property of Sn²⁺ to oxidise rapidly to Sn⁴⁺ in the presence of oxygen [69]. However, fabrication of a complete cell was successful while in the nitrogen environment. Despite the stability issues, the study also mentioned the possibility of Pb-free perovskite to be employed in perovskite solar cells with toxicology advantage over the Pb-based perovskite solar cells.

In comparison towards Pb-based perovskite absorber, a research has compared the properties (crystal structure, optical properties and charge transporting properties) of Pb-based and Sn-based of methylammonium (MA) and formamidinium (FA) halide perovskite, respectively [92]. It was demonstrated that the band gaps were ranging from 1.1 to 1.7 eV and showed excellent photoluminescence properties suitable for solar cell applications. Although the oxidation of Sn²⁺ to Sn⁴⁺ was also observed here, improved stability with high electron and hole motilities was recorded which shown potential towards Pb-free absorber layer. When Pb and Sn is applied simultaneously (MAPb_{1-x}Sn_xI₃) in the absorber layer, it was found out that the band gap values do not behave consistently with the increase in substitution rate [79]. At low concentration of Sn, the band gap decreases, then minimum band gap value at $x=0.5$ and 0.75, and lastly increases to 1.30 V when

Table 2 Research on lead free perovskite and its performance

References	Device description	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
[77]	Combination of formamidinium tin iodide with methylammonium lead iodide in inverted PSC	26.86	0.795	70.6	15.08
[78]	Mixed Sn/Pb perovskite in mesoscopic PSC and P3HT as HTM	20.04	0.42	0.5	4.18
[79]	Mixed Sn/Pb perovskite with mesoscopic PSC and spiro-MeOTAD as HTM	20.64	0.584	60.32	7.27
[80]	Cesium Tin iodide in mesoscopic PSC with SnF ₂ metallic control layer	22.70	0.24	0.37	2.02
[81]	Impact of anionic Br substitution in cesium tin iodide PSC	15.06	0.289	0.38	1.67
[82]	Application of cesium tin perovskite in planar structure	12.30	0.430	0.395	2.13
[83]	Formamidinium tin bromide perovskite in inverted structure	6.82	0.467	0.540	1.72
[84]	Cesium germanium iodide perovskite in mesoscopic PSC	5.7	0.074	0.27	0.11
[85]	Ratio of anionic Cl/Br modification in methylammonium Cupric PSC	0.216	0.256	0.32	0.017
[86]	Bismuth-based perovskite in mesoscopic PSC with P3HT as HTM	1.157	0.354	0.464	0.190
[87]	Bismuth-based perovskite in mesoscopic PSC with spiro-MeOTAD as HTM	0.52	0.68	0.33	0.12

Pb-free perovskite was tested. When the perovskite solar cells were fabricated, lead-free device was performing at 5.44% efficiency compared to Pb-based device at 8.31%. Additionally, it was mentioned that since the absorber layer showed activation towards near-IR region, it can be beneficial in both single junction and in tandem architecture where the band gap is required to be near 1 eV [93]. On the other hand, investigation on mixed halide Sn-based perovskite $\text{MASn}_{1-x}\text{I}_3\text{Br}_x$ showed an increasing energy band gap values towards higher Br-content (1.30–2.15 eV) [48]. Figure 4a shows the mesoscopic structure of the solar cell device with the colour change in different absorber layers on the right panel. It was stated that the lighter colours of the larger band gaps are attributed by the narrowed light absorption range of the absorber (Fig. 4b). It was reported that the higher Br-content absorber possess higher open circuit voltage (V_{oc}) and a lower short-circuit photocurrent density (J_{sc}). Most importantly, the spontaneous decomposition of the absorber layer were reported with

36% reduction in performance while stored in nitrogen environment and encapsulated.

In addition to MA and FA halide perovskite absorbers, Cs halide perovskite have also been investigated with Sn to study their compatibility [80, 81]. With lower energy band-gap of 1.3 eV, the CsSnI_3 perovskite absorber could harvest light at near-IR region and possess short-circuit photocurrent density of 34.3 mAcm^{-2} . It was mentioned that the metallic nature of the CsSnI_3 was alleviated by doping with 20% SnF_2 by reducing the background carrier density [80].

Organolead halide perovskite have also been investigated in inverted planar structure solar cells, with the usage of fullerene and its derivatives for the electron transporting layer, instead of inorganic metal oxide [94–96]. The incorporation of Sn has been reported by a study employing a structure of $\text{ITO/CuI/CsSnI}_3/\text{C}_{60}/\text{BCP}/\text{Al}$ [82]. The study also demonstrated the improvement in stability and performance using excess amount SnI_2 during the synthesis of CsSnI_3 . The excess amount of

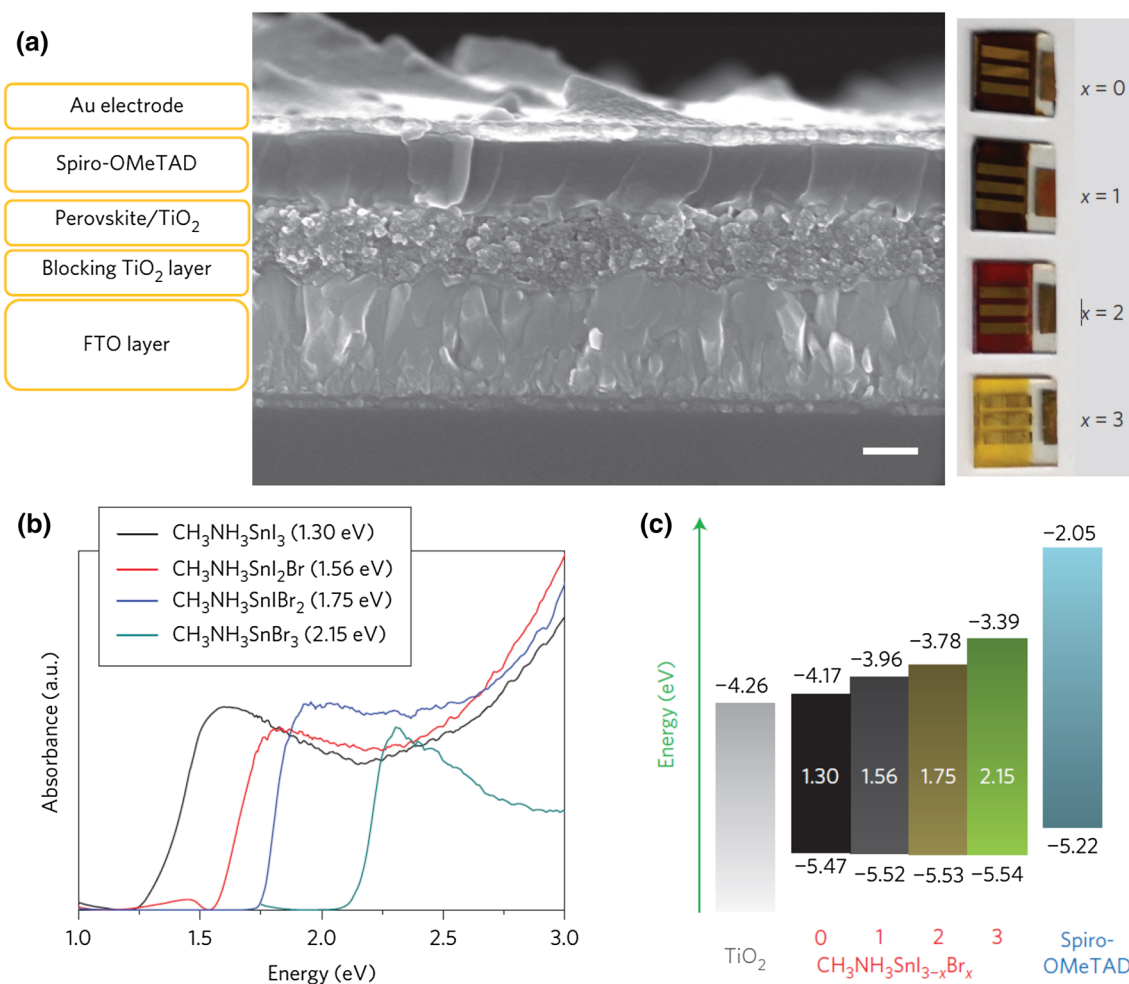


Fig. 4 **a** Perovskite solar cell device architecture with different absorber layer colour on the right panel. **b** Absorption spectra of the $\text{CH}_3\text{NH}_3\text{SnI}_{3-x}\text{Br}_x$ ($x = 0, 1, 2, 3$) perovskites. **c** Schematic energy-level diagram of $\text{CH}_3\text{NH}_3\text{SnI}_{3-x}\text{Br}_x$ with TiO_2 and spiro-OMeTAD HTM

SnI_2 is postulated to be able to minimize the Sn vacancy defects of the tin-halide perovskite which contributes to the metallic nature of Sn. Low temperature processing was utilized in the fabrication of solar cell devices with inverted planar structure of ITO/PEDOT:PSS/ $\text{FASnI}_2\text{Br}/\text{C}_{60}/\text{Ca}/\text{Al}$ [83]. With a combination of FASnI_2Br (band-gap of 1.68 eV) and low temperature annealing (75 °C), a power conversion efficiency of 1.72% was achieved with maintaining more than 60% performance efficiency after 30 h in nitrogen environment.

Ge-based perovskite have shown some potential as the absorber layer for photovoltaic solar cells based on density functional theory [97]. The study had prepared a series of Ge-based perovskite using Cs, MA, FA, acetamidinium, guanidinium, trimethylammonium, and isopropylammonium, to evaluate their potential as a perovskite absorber layer. It was demonstrated that these materials possess slightly higher bandgaps than the Pb counterparts, however, the problem of material stability is also present. It was demonstrated that the Ge-based perovskite performance in V_{oc} was poor and the recorded efficiency was only 0.2% [84].

Cu-based perovskite have also received attention due to its stability in air [98, 99]. Compared to the 3D perovskites, Cu-based perovskite are 2D with multi quantum-well electronic structure, presenting particular electronic, magnetic and dielectric properties [85, 88, 98, 100]. A study had fabricated Cu-based solar cells using $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{CuBr}_4$ and $(\text{F}-\text{C}_8\text{H}_8\text{NH}_3)_2\text{CuBr}_4$, with power conversion efficiency of 0.63 and 0.51%, respectively [98]. A study was focusing on the Br/Cl ratio to tune the light adsorption properties of Cu-based perovskite [99]. The study had postulated that the poor power conversion efficiency obtained was contributed by low absorption coefficient and heavy mass for the holes.

Bi-based perovskite, $\text{A}_3\text{Bi}_2\text{X}_9$ has attracted considerable attention due to its interesting properties [72, 86, 87, 101–104]. Bi-based perovskite have excellent stability towards moisture and less toxic compared to Pb-based perovskite. The 0D perovskite is formed due to bioctahedral $(\text{Bi}_2\text{I}_9)^{3-}$ clusters and the surrounding cations, as shown in Fig. 5. Previous study has demonstrated the stability of $\text{MA}_3\text{Bi}_2\text{I}_9$ in ambient environment for more than 40 days [72]. Nevertheless, the performance efficiency was sub-par with conventional structure (0.19%) and inverted planar structure (0.1%) [86, 87]. On the other hand, $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite had performed slightly better at 1.09% efficiency [72]. The performance of Bi-based perovskite is not as high as its Pb counterparts. Nevertheless, its potential as a less toxic alternative with high stability is expected to present some improvement in performance efficiency in the near future.

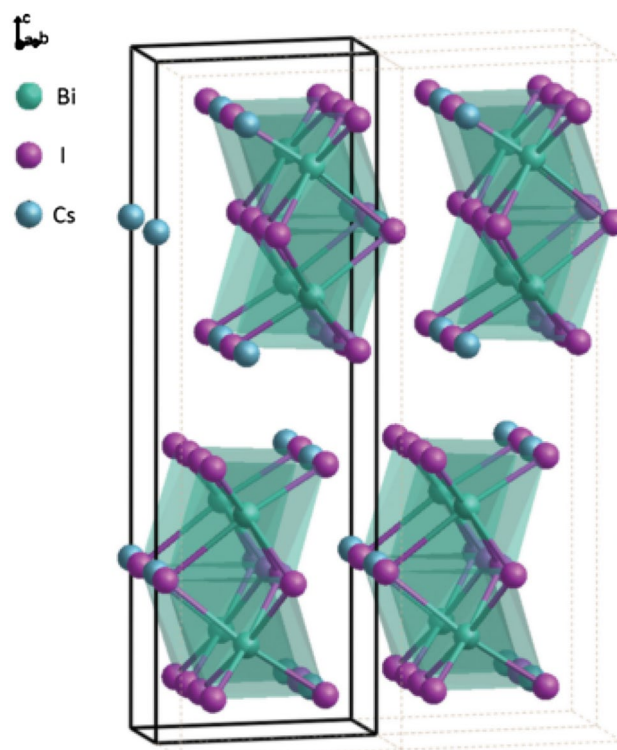


Fig. 5 Schematic diagram of Bi-based perovskite ($\text{Cs}_3\text{Bi}_2\text{I}_9$)

Conclusion and future prospect

In conclusion, this review concerns the material stability of Pb-based perovskite and the alternative replacement for Pb-based perovskite in photovoltaic solar cells. In the effort to manage the material instability of Pb-based perovskite, researcher often opt for improving fabrication technique or simply replace the Pb-based perovskite with alternative material. Although several materials have been proposed, most of them either still possess some extend of stability or inherently produce low performance efficiency. Developing suitable encapsulation technique may be relevant towards enhancing perovskite resistivity towards moisture. Material selection at the ETM and HTM may also contribute to a higher performance efficiency. Although the performance efficiency of Pb-alternative perovskite is still relatively low, the study is still at its infancy. Progress is expected at this study due to the less toxic with high stability perovskite available. Research output are expected towards this aim which may transform perovskite solar cells toward a truly green, highly stable and low-cost photovoltaic solar cells.

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